

Robust half-metallic ferromagnetism in the zincblende CrSb

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Using the accurate first-principle method within density-functional theory, we systematically study CrSb in the zincblende (zb) structure. The zb CrSb is predicted of robust half-metallic ferromagnetism (HMFM) with a magnetic moment of $3.000\mu_B$ per formula. It is much better than other zb compounds with HMFM because its spin-flip gap reaches 0.774 eV at the equilibrium volume and persists nonzero with its volume changing theoretically from -21% to $+60\%$. It is found there may be a common mechanism for the HMFM in all the zb Cr- and Mn-pnictides. Since being compatible with the *III-V* semiconductors, this excellent HMFM of the zb CrSb should be useful in spin electronics and other applications.

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Introduction. Half-metallic (HM) ferromagnets are absorbing more and more attention around the world, because they have only one electronic spin channel at the Fermi energy and should act as ideal components of spintronics devices [1,2]. Since de Groot *et al* first predicted HM ferromagnetism in Heusler compounds [3,4] in 1983, several HM ferromagnets, such as NiMnSb [5], CrO₂ [6], Fe₃O₄ [7], and the manganate materials [8], have been theoretically predicted and then experimentally confirmed. Much effort has been paid to understand the mechanism behind the HM magnetism and to study its implication in various physical properties [9]. At the same time it is still very important to find new HM ferromagnets which are more promising for basic properties and applications. [10]

Recently, much theoretical and experimental attention is paid to the HM ferromagnetism in the zincblende (zb) compounds such as *MA*s and *MSb* (*M* is a transition-metal element) [11,12,13,14,15,16], which are structurally and chemically compatible with the important *III-V* and *II-VI* semiconductors. The zb MnAs was theoretically predicted to be of so-called ‘nearly HM’ ferromagnetism [17]. Its Fermi level crosses the majority-spin (MAS) energy bands but touches the bottom of the minority-spin (MIS) conduction bands, and therefore there is no gap for spin-flip excitations in this case. Accurate calculations within density-functional theory (DFT) showed that the zb MnSb and MnBi are of true HM ferromagnetism [18]. On the other hand, it was already found that the zb CrAs is a true HM ferromagnet with a finite spin-flip gap [13,19]. Although crystalizing into the NiAs (na) phases in bulk form [20], the zb phases of CrAs [13,14], CrSb [15] and MnAs [12] have been successfully fabricated in form of thin films, multilayers or nanostructures on the *III-V* semiconductors. It is very interesting to find new HM ferromagnets with not only the same crystalline structure but also much more promising properties.

In this paper we systematically study CrSb in the zb structure with the accurate full-potential (linear)

augmented plane wave plus local orbitals (FLAPWLO) method within density-functional theory, and thereby predict that it is a true HM ferromagnet with a magnetic moment of $3.000\mu_B$ per formula. Being much more advantageous than the zb CrAs and Mn-pnictides, its theoretical spin-flip gap reaches 0.774 eV at equilibrium volume and persists nonzero with its volume changing from -21% to $+60\%$. Because not only the zb CrAs films of 5-6 unit cells (30 Å) in thickness [13,14] but also the zb CrSb thin films of 2 unit cells in thickness [15] have been successfully fabricated by means of epitaxial growth, the high-quality zb ferromagnetic (FM) CrSb films (and multilayers) of more than 5 unit cells in thickness [15] are believed to be obtained in the same way in the near future and therefore realize the prediction. It is also found there may be a common mechanism, which is similar to that of the Heusler by de Groot *et al*, for the HM ferromagnetism in all the zb Cr- and Mn-pnictides. Because being compatible with the *III-V* semiconductors, the robust zb HM FM phase of CrSb should be useful in spin electronics and in other applications.

Computational details. We make use of the Vienna package WIEN2k [21] for FLAPWLO method within density functional theory (DFT) [22] for all our calculations. As for the EC potentials, we mainly took the PBE96 [23] version for the generalized gradient approximation (GGA), but other versions of GGA and local spin density approximation (LSDA) [24] were also used for comparison and confirmation. The relativistic effect was taken into account in the scalar style, but the spin-orbit coupling was neglected in the results presented in this paper because it has little effect on the main results. We always used 3000 k-points in the Brillouin Zone, took $R_{mt} * K_{max}$ as 8.0 and made the expansion up to $l = 10$ in the muffin tins. The radii R_{mt} of the muffin tins was chosen to be approximately proportional to the corresponding ionic radii and as large as possible until reaching 2.3 (Cr) and 2.8 (Sb) Bohr, respectively. They were kept equivalent for different phases at their equilibrium

FIG. 2. The spin-dependent total density of states (DOS) of the equilibrium zb phase. The upper part denotes the majority-spin (MAS) DOS and the lower part the minority-spin (MIS) DOS. The bottom (U) of the MIS conduction bands is 0.872 eV and the top (L) of the MIS valence bands -0.774 eV, with the spin-flip gap being 0.774 eV.

In Fig. 2 we present the spin-dependent total DOS for the zb CrSb phase at its equilibrium volume. The upper part is for the MAS total DOS between -5 and 7 eV and the lower part the MIS. It is clear that the MAS electrons are metallic but there is a gap of 1.646 eV around the Fermi energy for the MIS electronic bands. The bottom (U) of the MIS conduction bands is at +0.872 eV and the top (L) of the valence MIS bands at -0.774 eV. The gap for creating an MIS hole at the top of the MIS valence bands by exciting an MIS electron into the conducting MAS bands is 0.774 eV and the gap for an MIS electron at the bottom of the MIS conduction bands is 0.872 eV. As a result, the minimal energy gap for a spin-flip excitation, or the HM gap, is 0.774 eV. This nonzero gap is essential to form a true HM ferromagnet. Fig. 3 demonstrates the corresponding energy bands in the high-symmetrical directions. There are 3 MIS and 5 MAS full-filled bands above -5 eV. The Γ_1 bands, corresponding to the Cr s states, are pushed above the Fermi energy by the interaction with the Sb s electrons. The three filled MIS bands (Γ_{15}) and the three filled MAS bands (Γ_{15}) reflect

FIG. 3. The spin-dependent energy bands of the equilibrium zb phase. The right panel is for the majority-spin (MAS) bands and the left the minority-spin (MIS) bands. There are three full-filled MIS bands and five full-filled MAS bands above -5 eV. There are only two partly-filled MAS bands, which together contribute 1 μ_B to the total moment per formula.

How does the HM ferromagnetism form? The Cr s states have moved above the Fermi energy because they must be orthogonal with the Sb 5s states [18]. It is shown by comparing the spin-dependent partial DOS, partial charge density and band structures that the two triplet band clusters in B and B' both result from the bonding of the Sb p and Cr d t_{2g} triplet electrons. There are approximately 2 and 2.6 Sb p (and 1 and 0.4 Cr d t_{2g}) electrons in B and B', respectively. On the other hand, the Cr d e_g states do not bond with Sb so that there exist two very narrow MAS bands (A) at -1.15 eV and the two MIS bands (A') around 1.7 eV. They are dominantly of Cr d e_g character, and are separated 2.85 eV from each other due to the exchange interaction. This exchange splitting is consistent with Im in the Stoner theory if we take $I \approx 1$ eV for the exchange integration and $m = 3$ for the present case. This kind of exchange splitting usually is enough to produce ferromagnetism in traditional ferromagnets such as bcc Fe, but, in addition, other en-

ergy bands must be of right structures at right positions in order to form HM ferromagnetism. In the case of the zb CrSb, the excellent HM ferromagnetism is formed because (1) The large exchange splitting of the narrow e_g bands pushes the MIS bands in A' above the Fermi energy, opening the MIS gap at the Fermi energy, and at the same time pulls the MAS e_g bands in A below the Fermi energy; (2) The presence of the Sb 5s electrons pushes the extended Cr 4s states above the e_g bands, keeping the MIS gap clean through avoiding them from mixing with the Cr d bands; (3) The triplet bands in C are partly filled with 1 electron per formula in order to conserve the total number of the electrons. The Cr t_{2g} states form polarly covalent bonds with the Sb 5p states so that approximate 1.5 electrons per formula are transferred towards the Sb sites. This enhances the Cr d exchange splitting and pins the Fermi energy at the right position through guaranteeing that the e_g bands remain very narrow and the DOS at the bottom of the bands in C is large enough. This explanation is similar to that by de Groot *et al* in their cases [3,4]. The difference is mainly in the role played by the Sb 5s electrons.

Comparing with the zb CrAs and the Mn pnictides, we find their energy band structures to be similar to that of the zb CrSb. It is observed in all these cases that (1) the Γ_1 bands are above the narrow Γ_{12} bands in band clusters A and A', (2) the Fermi energies are in the MIS band gaps formed between the empty MIS Γ_{12} in A' and the full-filled MIS Γ_{15} bands in B', and (3) the corresponding MAS Γ_{15} in B and Γ_{12} bands in A are all full-filled. The difference relies only on the relative positions of the Γ_1 bands and the Γ_{15} bands in C and C'. This means that the mechanism behind the HM ferromagnetism should be the same for all the zb Cr- and Mn-pnictides. It appears to be also the same as that in the Heusler compounds by de Groot *et al* [3,4]. It is very interesting that the mechanism behind the half-metallic ferromagnetism is the same in many cases, if not in all cases.

Is the HM ferromagnetism theoretically robust? The spin-flip gap, the essential characteristic for HM ferromagnetism, persists nonzero even when we theoretically change the cell volume from -21 % and 60 %. During this volume change, the MIS gap changes little, but the spin-flip gap decreases with the cell deviating from the equilibrium volume. The Fermi energy moves upwards when the volume decreases, but downwards when the volume increases. Its theoretical spin-flip gap, 0.774 eV, is much wider than 0.46 eV of the zb CrAs, 0.2 eV of the zb MnSb, and 0 eV of the zb MnAs. Its HM ferromagnetism survives from the large theoretical volume changes, being much more robust than the zb CrAs between (-15 %, +27 %) and the zb MnSb between (-6 %, +12 %). It is clearly much better than other known HM or nearly HM ferromagnetism in the zb compounds. We already confirmed the main results by using other EC potentials and parameters. Because of physical errors in the GGA

potential, there should be some calculation errors, but the relative volume error must be less than 10 % in these accurate full-potential DFT calculations. Anyway, since persisting for the volume changes from -21% to +60%, the HM ferromagnetism in the zb CrSb is indeed robust against any theoretical errors, even more robust when taking into account the fact that all real DFT calculations underestimate energy gaps.

What does this accurate DFT prediction imply for real zb CrSb materials? Because the zb CrSb is theoretically 1 eV unstable with respect to the ground-state phase, it has been realized only in form of thin films through epitaxial growth on the *III-V* semiconductors [15]. Anyway, the zb CrAs is also theoretically 0.9 eV unstable with respect to the na CrAs phase, but the zb CrAs thin films with 5-6 unit cells in thickness [13] have been successfully fabricated. This success makes us believe that one can successfully fabricate in the near future the high-quality zb CrSb thin films with more than 5 unit cells in thickness and similar zb multilayers. When the thickness of a zb CrSb film sample is larger than 5 unit cells, the prediction, based on the accurate DFT crystal calculation, must apply to their internal parts deep beyond 2 unit cells, where there is very little surface effect. The real spin-flip gap should be approximately 1 eV because all LSDA and GGA calculations within DFT usually underestimate the gap by 30 - 60 %. A wide spin-flip gap implies that nearly 100 % spin polarization can be achieved at quite high temperature. The zb CrSb of the HM ferromagnetism may be the only candidate, which not only has excellent robust HM ferromagnetism but also shares the same crystalline structure as the important *III-V* semiconductors, and therefore, should be useful in spin electronics and in fabricating HM magnetic quantum wells, dots and multilayers with some of them.

In summary, we systematically study CrSb in the zb structure with the full-potential LAPW method within density-functional theory, and thereby predict that it is a robust HM ferromagnet with a magnetic moment of $3.000\mu_B$ per formula. The large exchange splitting of the narrow Cr e_g bands is essential in forming its ferromagnetism. The presence of the low-lying Sb 5s electrons and the polar-covalent bonding between the Sb p and Cr t_{2g} states both are necessary in further forming its half-metallic characteristic. It is found there may be a common mechanism for the HM ferromagnetism in all the cases of the zb Cr- and Mn-pnictides. Its excellent spin-flip gap makes it possible to achieve nearly-full spin polarization at high temperature. The HM ferromagnetic phase of the zb CrSb is much better than those of the other zb compounds, and therefore should be useful in spin electronics and other applications because being compatible with the important *III-V* semiconductors.

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